Dependence on light sources of the artificial photodegradation of wood

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The photodegradation in wood caused by sunshine is a complicated process. The intensity and wavelength content of sunlight depends on plenty of uncontrolled parameters. In addition these parameters are changing not only during a year but even within a day. This is the reason that artificial light sources are often used to clarify the mechanism of wood photodegradation. Some of these light sources can imitate the contents of sunlight, while the others emit only a part (or some parts) of the spectra emitted by the Sun.

The emission spectrum of the Sun is shown in Fig.1. The Ozone layer of the Earth filters some parts of the emitted light (black area). An other part is scattered by the air. The energy distribution which can reach the surface of the Earth is presented by the dotted line.

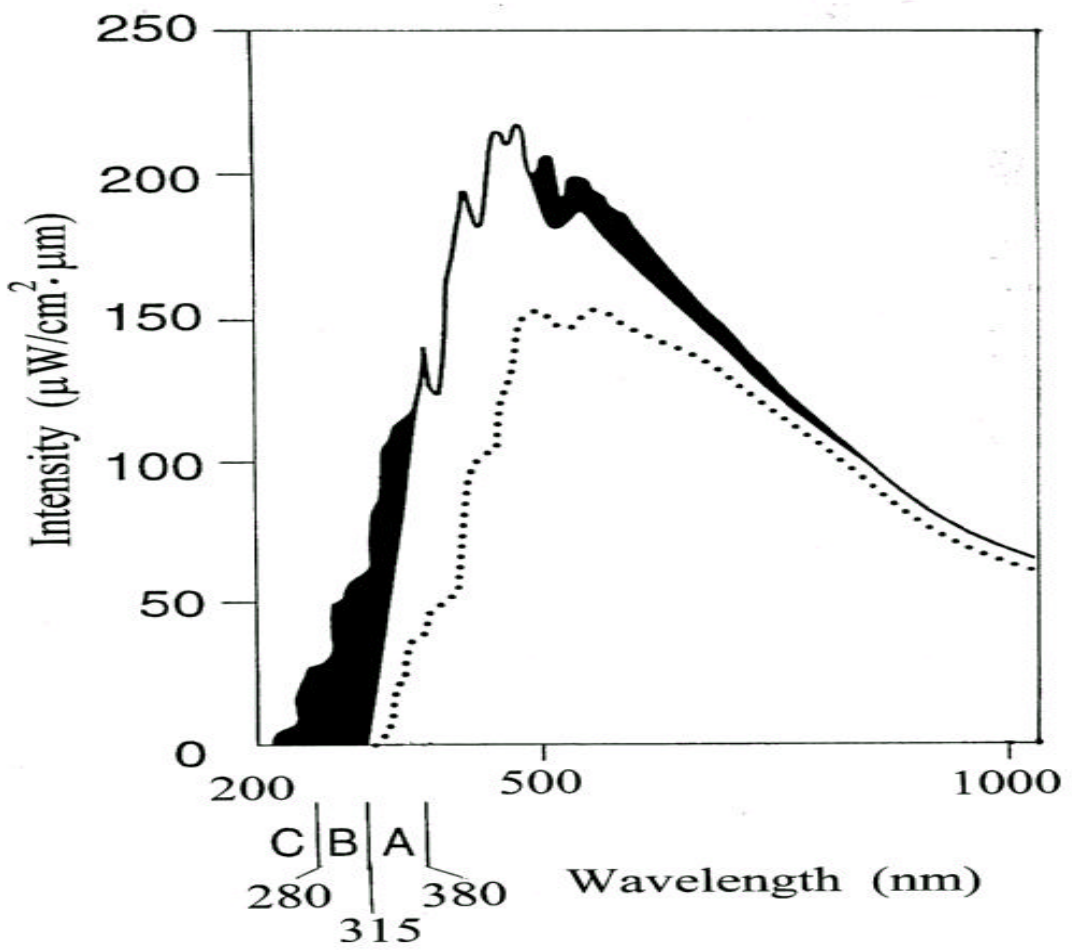

Fig. 1. The emission spectrum of the Sun. (The black area is filtered by the Ozone layer.) The doted line represents the light intensity distribution on the surface of the Earth.

For photodegradation the ultra violet (UV) part (?<380nm) is the most effective wavelength region. Under normal condition only the "A" part of the UV light can go through the air. If the Ozone layer is thinner even missing the "B" and "C" parts also are able to reach the outdoor wooden materials. During artificial simulation of the sunlight the UV "B" part also need to take into consideration. The spectrum of the Xenon lamp is similar to the spectrum of the Sun. The only exception is that the spectrum of Xenon lamp does not contain UV "B" and "C" parts. So the Xenon lamp can be recommended if the imitation of normal sunlight without UV "B" part is needed.

The spectrum of Mercury vapour lamp is presented in Fig. 2. This spectrum contains only soma narrow peaks. Most of peaks are in UV region covering all of parts (A;B;C). For the investigation of the UV photodegradation the Mercury lamp is recommended.

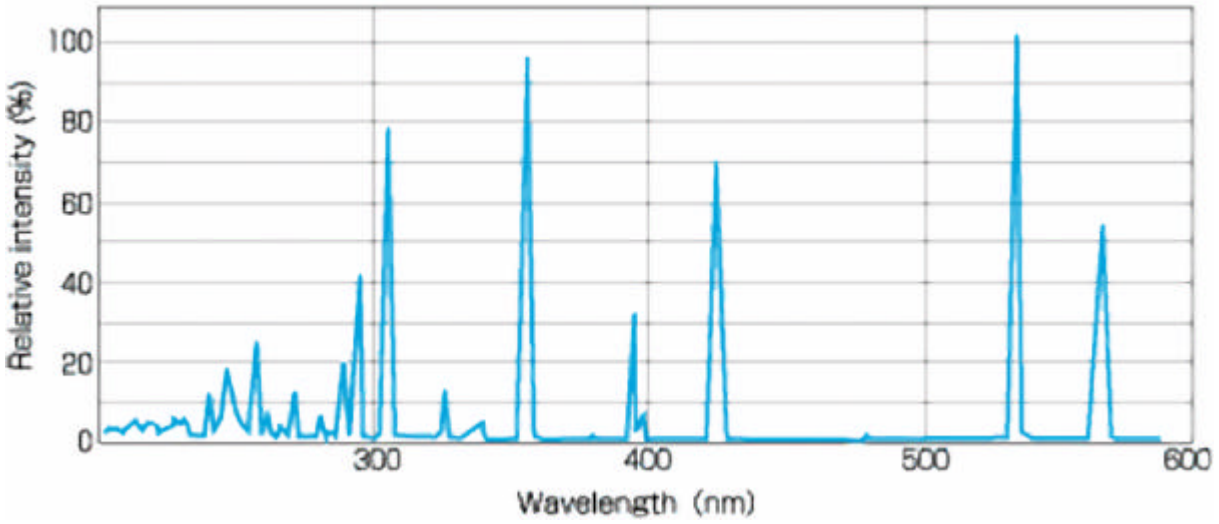

Fig. 2. The emission spectrum of Mercury vapour lamp

The chemical changes of wood caused by photodegradation are mostly monitored by infra red (IR) spectroscopy and by colour measurement. The colour data are usually given in CIELAB colour co-ordinate system. Fig. 3. presents the colour changes of black locust (*Robinia pseudoacacia*) caused by Xenon lamp, Mercury vapour lamp, heat treatment at 90^0C under 100 % relative air humidity and under total dry condition, respectively. The total duration of all treatments were 200 hours. (The a* values represent the red colour and the b* values the yellow colour part of the samples.) The natural black locust wood has yellow colour represented by high b* value and low a* value. These are the starting points on the left side. The right end represent the effect of 200 hours treatment. Both of light treatment changed the colour of the samples towards red, considerably. The yellow content slightly increased. The Mercury lamp made continuos yellowing in contrast to the xenon lamp where the yellowing started after 40 hours of exposure.

During irradiation by Xenon lamp the half part of the sample was cowered by a metal plate to prevent the light irradiation. The colour of the covered area after 200 hours of treatment is represented by the "**?** " marked dot. This colour change towards red was created by the heat degradation. This thermal degradation was simulated with thermal treatment at 90^0C under dry

and humid conditions. (The colour change under natural conditions is between these two changes.) The thermal treatment changed the colour towards red in both cases and decreased the yellow content with rising air humidity. It can conclude, Xenon lamp makes thermal degradation too which must be taken into consideration during the test.

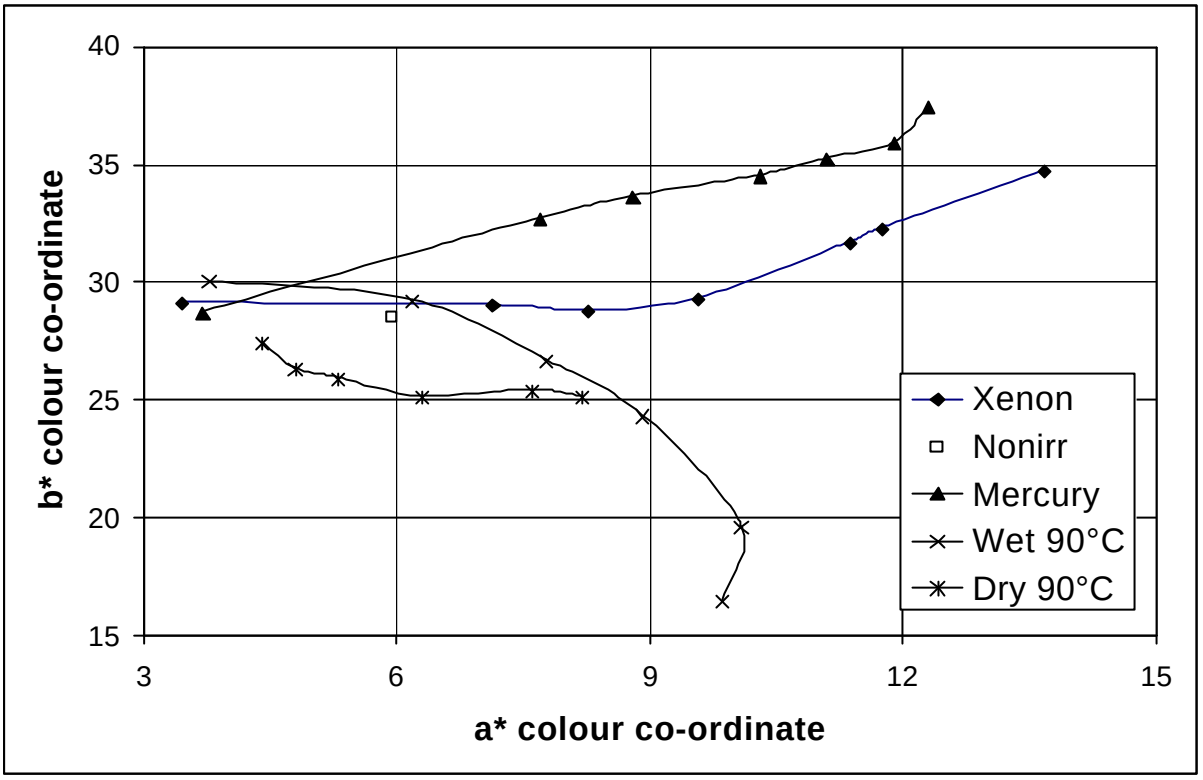

Fig. 3. Colour changes of black locust wood samples caused by different irradiations.

The most useful analytical tool for chemical analysis of wood photodegradation is the IR spectroscopy. Regarding the wood is an excellent light absorber and the photodegradation is a surface phenomenon only the diffuse reflectance Fourier transform (DRIFT) technique can be successfully applied. Fig. 4 represents a typical DRIFT spectrum of Scots pine (*Pinus silvestris*). These intensities include both of absorption and scattering. The scattering does not sow wavelength dependence in the examined region, so the shape of the DRIFT spectrum is similar to the absorption spectrum. The DRIFT spectrum is usually presented as the absorption spectrum. All of peaks represent the IR light absorption of different chemical groups. The IR spectrum of the wood is rather combined because of the extremely complicated chemical structure of the wood material. The 1000-1800 cm^{-1} range is individual for all wood species. It is usually called as fingerprint domain.
The band assignment is given in Table 1.

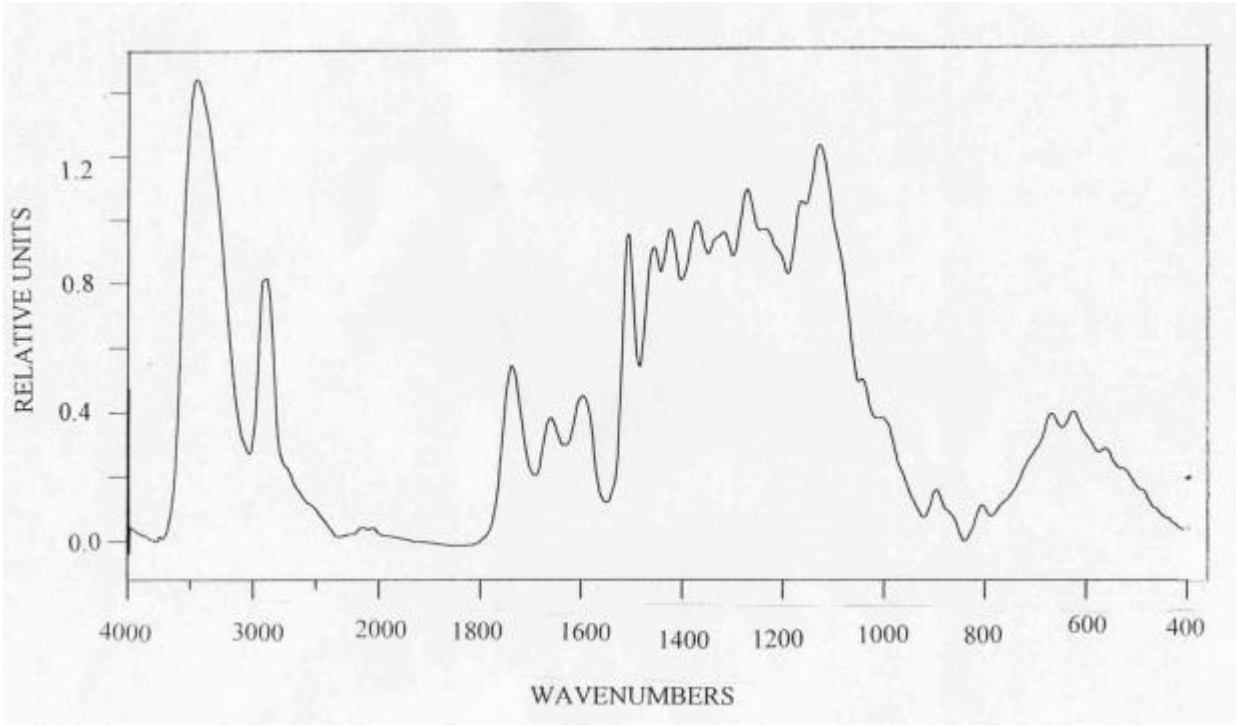

Fig. 4.DRIFT spectrum of Scots pine (earlywood part of sapwood)

Table 1. Band assignment of IR spectrum of Scots pine in wavenumbers (cm^{-1})

3468	OH stretching	1427	C-H deformation (asymm.)
2929	CH,CH_2 stretching (asymm.)	1373	C-H deformation (symm.)
2905	CH,CH_2 stretching (symm.)	1319	C-H deformation,CH_2 wagging
1740	CO stretching in unconjugated ketone, acetyl, carboxyl groups	1275	C_{aryl}-O, guaiacyl ring breathing with CO stretching
1662	H_2O,CO stretch. in conjugated syst	1170	C-O-C stretching (asymm.)
1598	aromatic skeletal breathing	1132	C-O-C stretch. (symm.), arom.C-H
1510	aromatic skeletal breathing	1003	C_{alkyl}-O
1457	C-H deformation (asymm.)	898	C-H deformation of cellulose

During the photodegradation of wood same chemical structures are destroyed and others are newly created presented by absorption decreases and increases, respectively. Fig. 5 shows the absorption changes of Scots pine (earlywood part of sapwood) during 200 hours of UV irradiation by Mercury vapour lamp. The most important part of IR spectrum is zoomed here. The irradiation was occasionally interrupted to determine the changes. During the irradiation the number of aromatic ring units of lignin decreased (absorption decrease at 1510 cm^{-1}) and

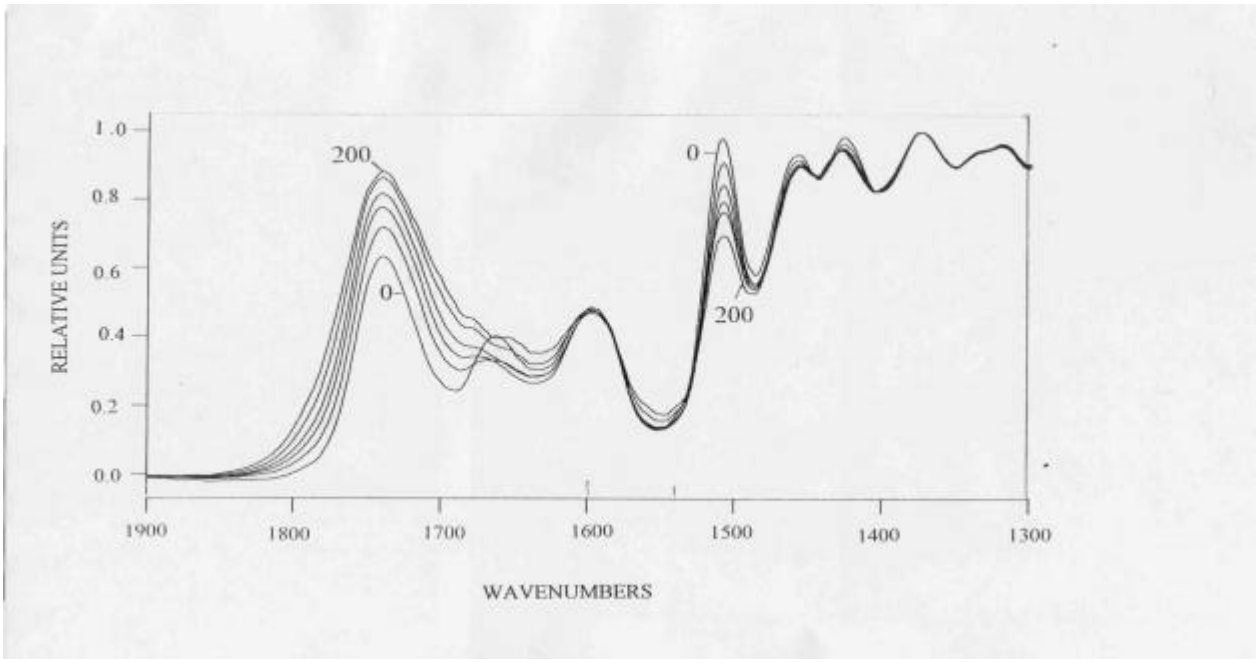

Fig. 5. Absorption spectra of Scots pine (earlywood part of sapwood) after 0; 10; 25; 50; 100; 200 hours of UV irradiation

the number of different carbonyl groups being in unconjugated position (absorbing around 1749 cm^{-1}) increased consequently. Comparing the spectra it can conclude one band decreased and one other increased. Calculating the difference spectrum (irradiated minus bulk) can be realised not only one peak increased but two close to each other (Fig.6.) at 1763 cm^{-1} and 1715 cm^{-1}.

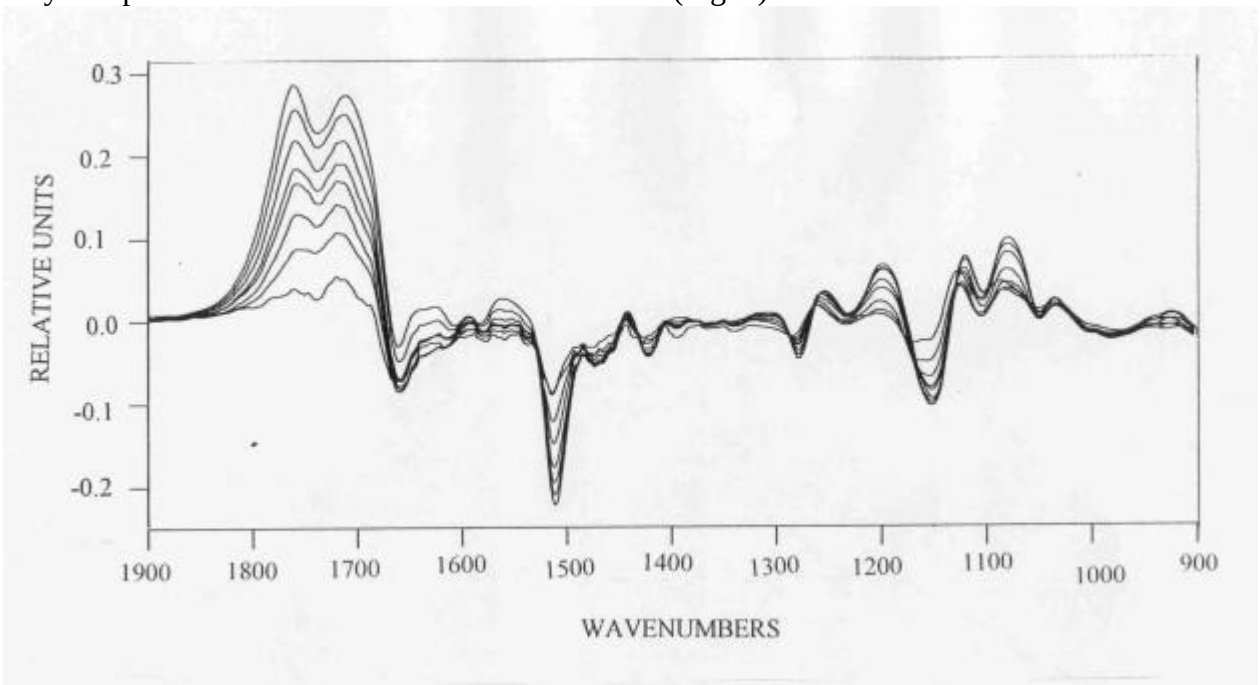

Fig. 6. Difference spectra of Scots pine (earlywood part of sapwood) after 5; 10; 17; 25; 50; 70; 100; 200 hours of UV irradiation

The difference spectrum presents only that peaks which have chanced during the treatment. It can give more detailed information than the visual comparison of the absorption spectra. This is the main advantage of the difference spectrum method, if there are plenty of peaks covering each other.

The effectivity of the difference spectrum method is well represented in Fig. 7 where the effect of 200 hours UV treatment is presented together with the effect of 24 hours of storage of irradiated samples under distilled water. The water leached out a part of the degradation products (negative peak at 1760 cm^{-1}). The curve in the middle represents the degradation products remaining in the wood after water leaching. Here is well presented the water leaching removes partly the different carbonyl groups (created during the photodegradation) but in different quantity.

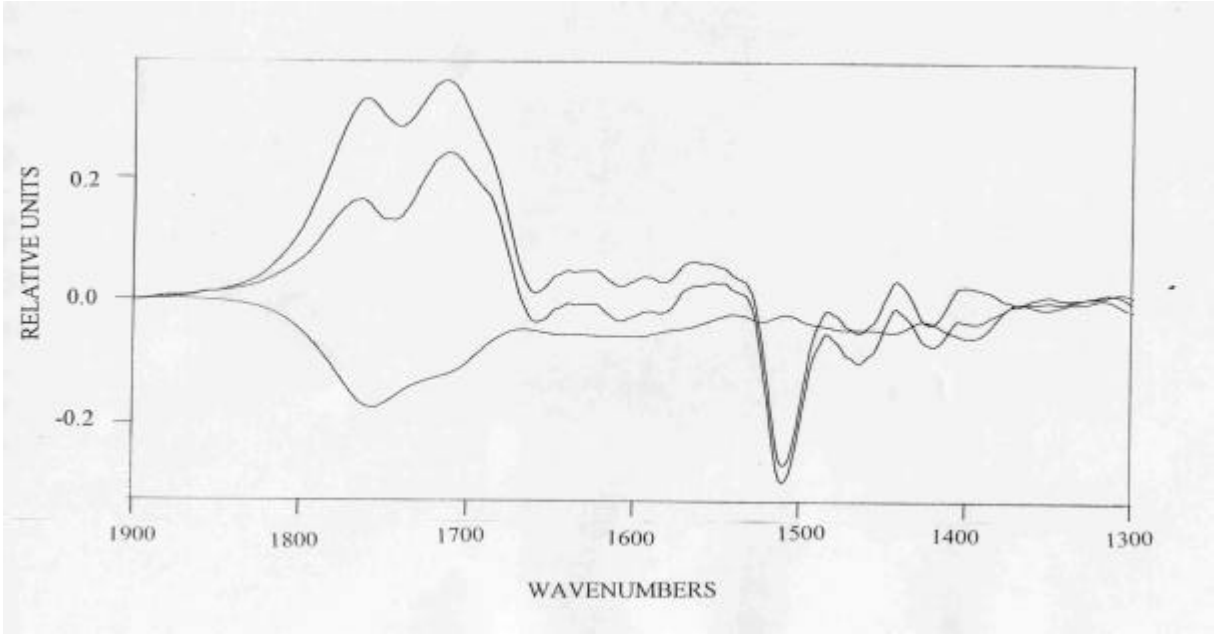

Fig. 7. Difference spectra of Scots pine (earlywood part of sapwood) after 200 hours of UV irradiation (top curve), followed by 24 hours of water leaching (negative peak at 1760 cm^{-1}), degradation products remaining in the wood after leaching (curve in the middle)

The difference spectrum method gives the possibility to present the differences between the UV photodegradation properties of different wood species. Fig. 8. represents the difference spectra of larch (*Larix decidua*), Scots pine, spruce (*Picea abies*), poplar (*Populus euram I-214*) and black locust wood species (earlywood part of sapwood) after 200 hours of UV irradiation. The fingerprint region is zoomed below to show the differences. The spectra of conifers are quite similar. The spectra of hardwoods present three main differences comparing to the softwoods. In C-O-C linkage region (1100-1200 cm^{-1}) the absorption increase and decrease are more pronounced at hardwoods than softwoods. In the absorption region of unconjugated carbonyl groups the two main absorption increases are closer to each other at poplar wood than softwoods. In the case of black locust the absorption increases of the

unconjugated carbonyl groups are smaller comparing to all of examined wood species and the peak at 1715 cm^{-1} is completely missing. There is small shoulder at 1700 cm^{-1} what can be seen at all cases. This shoulder becomes visible at black locust wood because of the missing neighbouring peak.

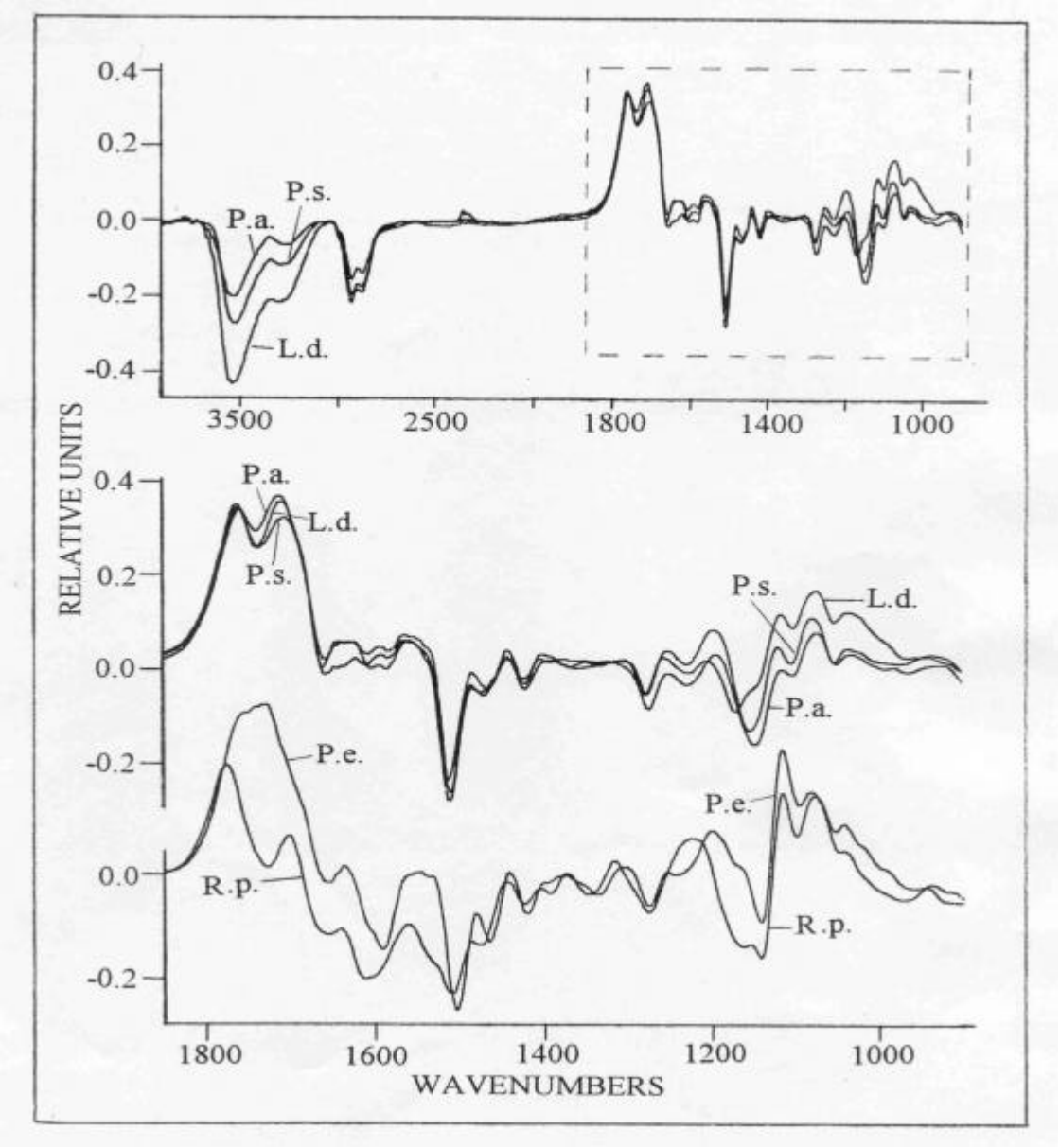

Fig. 8. Difference spectra of larch (L.d.), Scots pine (P.s.), spruce (P.a.), poplar (P.e.) and black locust (R.p.) wood species (earlywood part of sapwood) after 200 hours of UV irradiation

In focus of interest are recently the preliminary results of an ongoing project where the laser light-wood interactions are studied. The laser beam contains exactly one wavelength and the intensity of the beam can be measured exactly. The applied wavelengths were between 581 nm and 193 nm (this latest wavelength in not part of the sunlight which can reach the surface of the Earth.

Table 2 presents the physical parameters of the applied lasers. The wavelengths cover all of UV regions and represent all three parts (A; B; C) of it. The 581 nm is in the visible light region representing yellow colour. The total irradiation energy was set to 100 Joule in all cases. The only exemption the ArF laser was (emitting at 193 nm). In that case the surface of wood samples started to evaporate after 15 Joule of irradiation energy so the irradiation had to be interrupted here.

Table 2. Data of the applied lasers

Laser type	Wavelength (nm)	Impulse energy (mJoule)	Impulse time (ns)	Impulse frequency (Hz)	?Energy (Joule)
ArF	193	10	20	10	15
KrF	248,5	20	15	10	100
XeCl	308	20	20	10	100
Nitrogen	337	2,8	-	30	100
Rodamin	581	4	-	10	100

The equal energy irradiation and the exact wavelength give the opportunity to examine the wavelength dependence of wood photodegradation. Fig. 9. represents the difference IR spectra caused by laser irradiation at 248; 308 and 337 nm in the case of Scots pine (earlywood part of heartwood). The main chemical changes at 308 nm and 337 nm wavelengths of irradiation are similar to the changes caused by Mercury lamp. Differences can be seen in 1100-1200 cm^{-1} region. This is the absorption of the C-O-C linkage.

The irradiation at 248 nm was the most effective among the applied wavelengths. There were new absorption decreases around 1539; 1465 and 1396 cm^{-1} These changes have never been mentioned before. Beside the well known absorption increase in 1700-1800 cm^{-1} region (absorption of the unconjugated carbonyl groups) there was an intensive wide absorption increase around 1600 cm^{-1} which is the absorption region of the conjugated carbonyl groups.

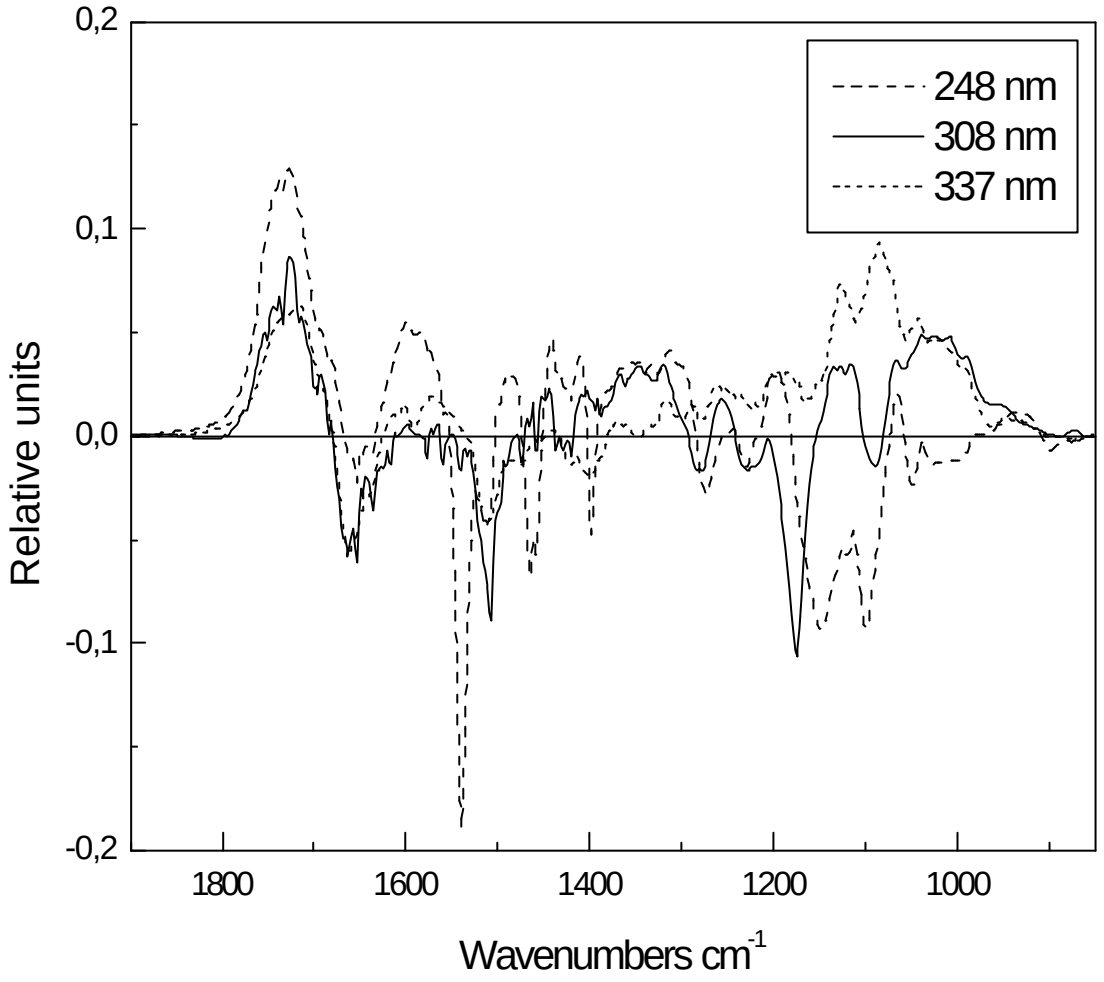

Fig. 9. Difference spectra of Scots pine (earlywood part of heartwood) after 100 Joule laser irradiation at 248; 308 and 337 nm

The irradiation at 193 nm and at 581 nm hardly gave any changes (Fig.10). It can be because of the applied law energy, or this type of photons du not make changes in lignin molecules. This problems need further investigation. These wavelengths could be the barriers of the effective area for photodegradation.

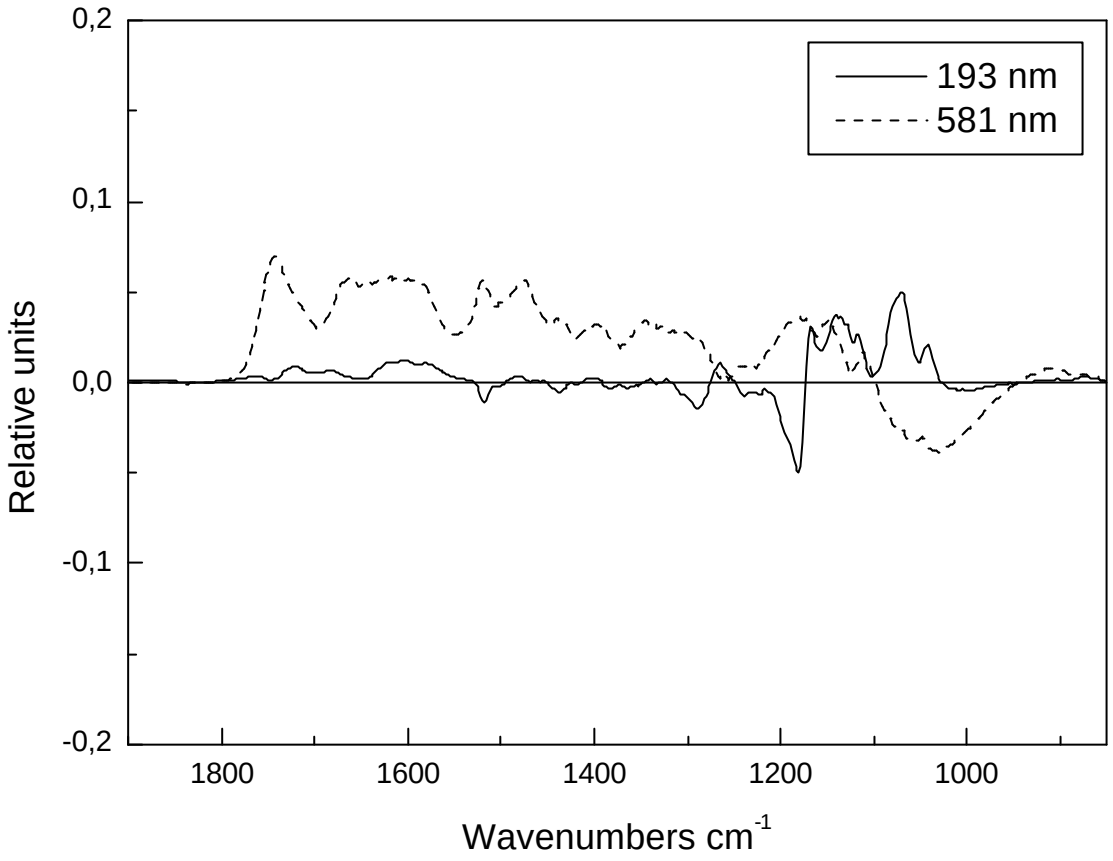

Fig. 10. Difference spectra of Scots pine (earlywood part of heartwood) after laser irradiation at 193 and 851 nm

The exact determination of irradiation energy and the difference spectrum method give the possibility to determine the degradation nature of the different wood tissues. These data of Scots pine are presented in Fig. 11-12. The earlywood part is more sensitive against photodegradation than the latewood, and the sapwood is also more sensitive than the heartwood. The degradation properties of earlywood parts are similar, but there are differences between latewood part of sapwood and heartwood. The main differences are in 1100-1200 cm^{-1} region and around 1750 cm^{-1}. These are the absorptions of the ether bonds and the unconjugated carbonyl groups, respectively. The change in ether bond system is similar to the changes caused by Mercury lamp at hardwoods (Fig. 8.).

Summarizing the results, we might conclude that the UV-laser not only causes the changes in the difference spectra of the wood samples that are also produced by the traditional UV-radiators, but also produces new decrease bands (1398, 1465, 1535 cm^{-1}) that have never been mentioned before. Further studies are necessary to explore the chemical changes taking place in wood as a result of UV-light that was produced by laser.

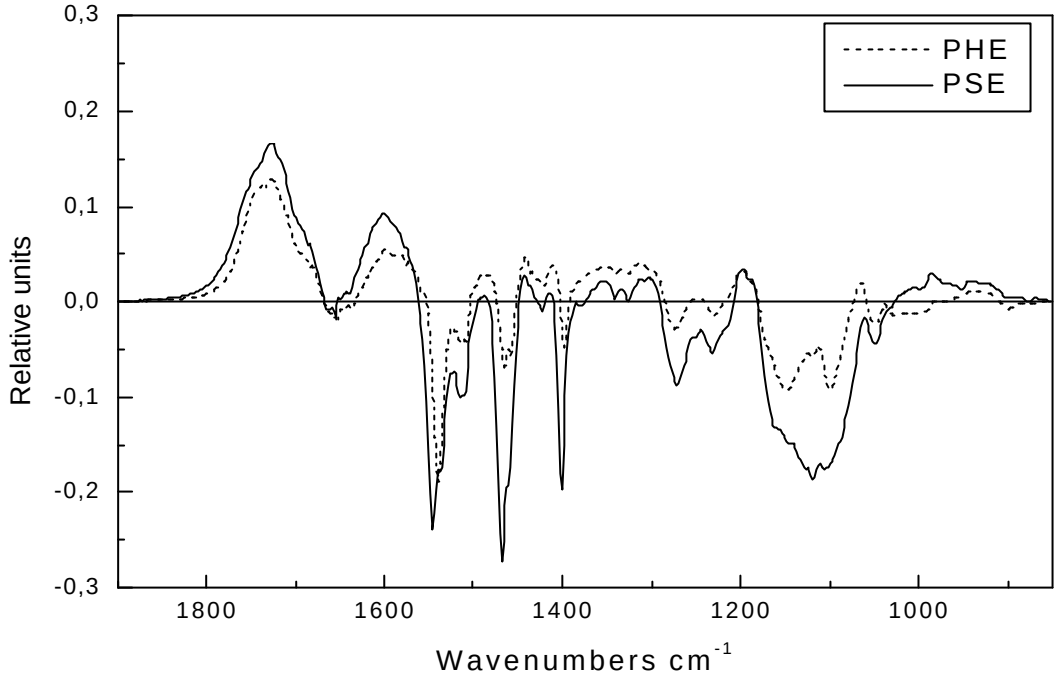

Fig. 11. Difference spectra of earlywood (E) parts of Scots pine (heartwood (H) and sapwood (S)) irradiated by 248 nm wavelength

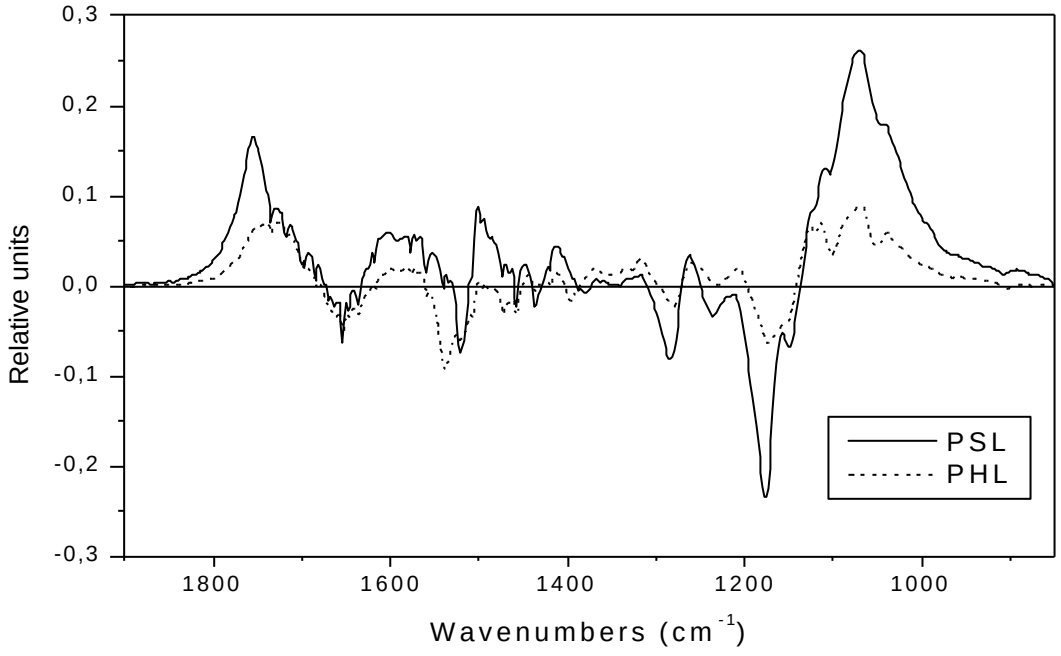

Fig. 12. Difference spectra of latewood (L) parts of Scots pine (heartwood (H) and sapwood (S)) irradiated by 248 nm wavelength